



## Short communication

## Investigation into the effects of sulfur on syngas reforming inside a solid oxide fuel cell



Ting Shuai Li<sup>a,\*</sup>, Min Xu<sup>a</sup>, Chongxin Gao<sup>a</sup>, Baoqing Wang<sup>a</sup>, Xiyun Liu<sup>a</sup>, Baihai Li<sup>a</sup>, Wei Guo Wang<sup>b</sup>

<sup>a</sup>School of Energy Science and Engineering, University of Electronic Science and Technology of China, 2006 Xiyuan Road, Chengdu, Sichuan, PR China

<sup>b</sup>Division of Fuel Cell and Energy Technology, Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences, 519 Zhuangshi Road, Ningbo 315201, China

## H I G H L I G H T S

- The durability of a fuel cell operated with simulated syngas is studied.
- The sulfur poisoning effects to the cell in syngas is investigated.
- The internal reforming of CH<sub>4</sub> is restrained by the presence of H<sub>2</sub>S.
- The sulfur poisoning impact is inhibited due to the steam in syngas.

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## A B S T R A C T

The electrochemical performance and long-term durability of a solid oxide fuel cell have been evaluated with a simulated coal syngas containing 2 ppm H<sub>2</sub>S as fuel. The resulting impedance spectra indicate that no observable power loss is caused by the addition of 2 ppm H<sub>2</sub>S, and the cell shows stability of nearly 500 h at 0.625 A cm<sup>-2</sup>. The composition of mixed gas is analyzed both at a current load of 0.625 A cm<sup>-2</sup> and open circuit state. Hydrogen and carbon monoxide are directly consumed as fuels at the anode side, whereas methane stays unchanged during the operation. It seems the internal carbohydrate reforming and impurity poisoning interacts and weakens the poisoning effects. The oxidation of H<sub>2</sub> and the water gas shift reaction take advantages over methane reforming at the cell operational conditions.

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## 1. Introduction

Integration of SOFC and coal gasification is expected to utilize the coal resource at a clean and efficient way [1]. Syngas are mainly comprised of hydrogen, carbon monoxide, carbon dioxide, steam, methane and various contaminants [2]. The largest obstacle for SOFC running on a coal derived syngas includes carbon deposition [3,4] and contamination of various impurities [5–7], leading to catalyst malfunction and microstructure degradation.

The features of sulfur impurity poisoning a nickel based SOFC was not only related to the operational temperatures [8], current densities [9] and sulfur concentrations [10], but it was also evidently impacted by fuel compositions. Tremblay et al. [11] studied

the effects of coal syngas and H<sub>2</sub>S on the performances of a single cell and a stack, where a mixture of 20% H<sub>2</sub>–33% CO–29% N<sub>2</sub>–18% H<sub>2</sub>O containing more than 200 ppm H<sub>2</sub>S induced a remarkable cell degradation. We reported the addition of steam was able to reduce the degree of large scale of sulfur poisoning a SOFC [12], whereas sulfur inside the anode domain would be trapped at the oxygen vacancy, which failed to be removed by clean fuel [13].

CH<sub>4</sub> was likely reformed with H<sub>2</sub>O and CO<sub>2</sub> to yield CO and H<sub>2</sub> (internal reforming), which could be straightforwardly utilized as reactants [14,15]. Since it was more difficult to electrochemically oxidize CO than H<sub>2</sub>, CO was possibly to react with H<sub>2</sub>O, producing CO<sub>2</sub> and H<sub>2</sub> (water gas shift reaction). Also, CO or CH<sub>4</sub> oxidizing reactions were strongly influenced by the H<sub>2</sub>S exposure [16]. The addition of 1 ppm H<sub>2</sub>S degraded the direct internal reforming of CH<sub>4</sub> [17]. Moreover, sulfur in fuels was in turn to retard the water gas shift reaction, causing cell degradation to different extents [18].

\* Corresponding author. Tel./fax: +86 028 61831080.

E-mail addresses: [litingshuai@uestc.edu.cn](mailto:litingshuai@uestc.edu.cn), [litingshuai@gmail.com](mailto:litingshuai@gmail.com) (T.S. Li).

Therefore, the durability of solid oxide fuel cells in a simulated coal-derived fuel containing sulfur should receive increasing attentions. The relevant reactions involving  $\text{CH}_4$  reforming, water gas shift reaction and  $\text{CO}/\text{H}_2$  oxidation is thermodynamically favorable at typical SOFC operational conditions, but the impurity is able to affect these reactions happening, abating the electrochemical performance. The aim of this investigation is to study the related mechanisms, which is expected to further interpret the interplay of internal reforming and sulfur poisoning Ni based fuel cells.

## 2. Experimental

A typical anode supported solid oxide fuel cell was tested in this study. Details of the cell had been narrated elsewhere [7]. The as-fabricated cell of  $100\text{ cm}^2$  was cut to a testing standard active dimension of  $16\text{ cm}^2$ . The cell was sealed in an alumina rig and was heated to  $850\text{ }^\circ\text{C}$  at a rate of  $1\text{ }^\circ\text{C min}^{-1}$ . It was then reduced in a pure hydrogen atmosphere for more than 5 h in order to completely reduce nickel oxide to nickel. Current–voltage ( $I$ – $V$ ) curves were characterized with hydrogen (500 sccm) and a syngas of 4%  $\text{CH}_4$ –5%  $\text{CO}$ –13%  $\text{CO}_2$ –48%  $\text{H}_2$ –30%  $\text{H}_2\text{O}$  (total 500 sccm) as fuels using a SOFC testing apparatus at  $800\text{ }^\circ\text{C}$ . The cathode was flowed with 2000 sccm air.

Electrochemical impedance spectra (EIS) were simultaneously measured applying an Im6ex electrochemical station (ZAHNER, Germany) with a scanning frequency ranges from 1 MHz to 0.1 Hz. Evolution of cell power was recorded with the syngas containing 2 ppm  $\text{H}_2\text{S}$ , meanwhile the gas composition was diagnosed using a proline mass spectrometer (AMETEK, USA) in an in-situ means at polarized and open circuit conditions. Post-mortem microstructure of the cell was observed after test using a Hitachi S4800 field emission scanning electron microscope (FE-SEM/EDS).

## 3. Results and discussion

The open circuit voltages (OCV) reach 1.06 V and 0.97 V as shown in Fig. 1 when the cell is fed with pure hydrogen and the syngas as fuels. The presence of 30% steam in syngas greatly reduces cell potential, which can be well understood in terms of the Nernst equation as expressed by Eq. (1), where  $P_{\text{O}_2(\text{cathode})}$  and  $P_{\text{O}_2(\text{anode})}$  denote the oxygen pressure at the cathode

$$\text{OCV} = \frac{RT}{4F} \ln \left( \frac{P_{\text{O}_2(\text{cathode})}}{P_{\text{O}_2(\text{anode})}} \right) \quad (1)$$

side and anode side,  $R$  and  $F$  are constants.  $P_{\text{O}_2(\text{cathode})}$  can be readily confirmed since the cathode is flowed with air, so the OCV value depends the most on  $P_{\text{O}_2(\text{anode})}$ , which is calculated to be  $4.27 \times 10^{-22}\text{ atm}$  when hydrogen is used as fuel, corresponding to 1.1 V for OCV. However, it is becoming more complicated to use one or two equations to compute the OCV for syngas due to the  $\text{CH}_4$  reforming and water gas shift reaction varying composition of the mixed gases. Anyway, the presence of steam and carbohydrate both increases the  $P_{\text{O}_2(\text{anode})}$ , leading to the OCV decrease.

The EIS of the cell measured both at the two atmospheres are depicted in Fig. 2, where the ohmic resistance is 10 mΩ and polarization part comes to around 30 mΩ. It is noted that no remarkable deviation occurs to the spectra with and without 2 ppm  $\text{H}_2\text{S}$  in Fig. 2. There are several related courses that may contribute to reduction of the  $\text{H}_2\text{S}$  poisoning effects to a SOFC. The presence of 30% steam not only participate in reforming hydrocarbon, but it can potentially reduce the sulfur adsorption and reactions with catalyst [12]. Besides, there are still other gas compositions including carbon monoxide and carbon dioxide that are capable of affecting the

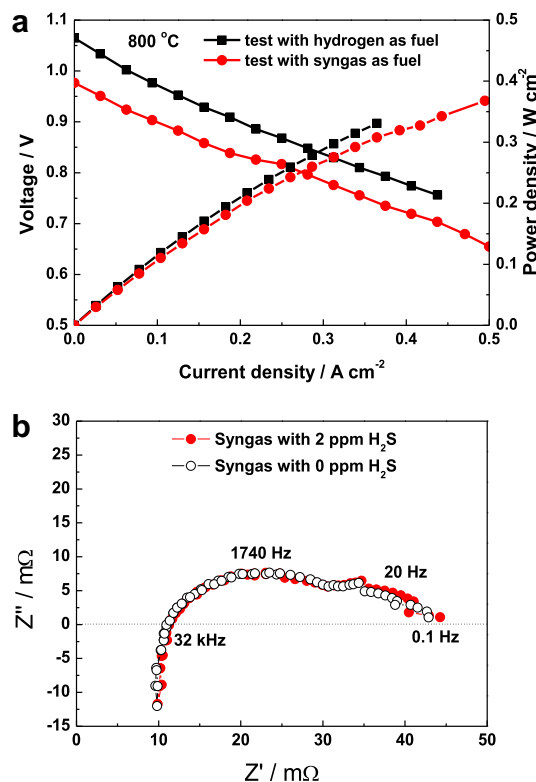


Fig. 1. Current and voltage curves of the cell tested at pure hydrogen and syngas at  $800\text{ }^\circ\text{C}$  (a), electrochemical impedance spectra measured at syngas with and without 2 ppm  $\text{H}_2\text{S}$  at  $800\text{ }^\circ\text{C}$  (b).

sulfur poisoning behavior [8,19]. Two separate arcs have been recorded in the impedance spectra, slight deviation happening at low frequencies ranges below 20 Hz, possibly pertinent to the gas diffusion and conversion at anode [20], indicating sulfur probably impacts the oxidation of fuels in the mixed gases

A minute power drop is observed at the two measuring stages of total 500 h' operation as demonstrated in Fig. 3. The area specific resistance (ASR) value is calculated by the equation  $\text{ASR} = (\text{OCV} - V_i)/i$ , which shows a relatively stable value during the operation. Meanwhile, the gas compositions are analyzed during this period both at a polarized and open-circuit state as shown in Fig. 4. An increase of relative content both occurs to  $\text{H}_2$  and  $\text{CO}$  after switching the cell from the  $0.625\text{ A cm}^{-2}$  load to an

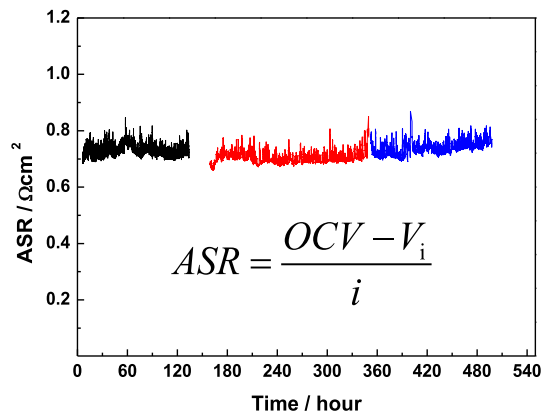


Fig. 2. Evolution of the cell power at syngas containing 2 ppm  $\text{H}_2\text{S}$  at  $800\text{ }^\circ\text{C}$ .

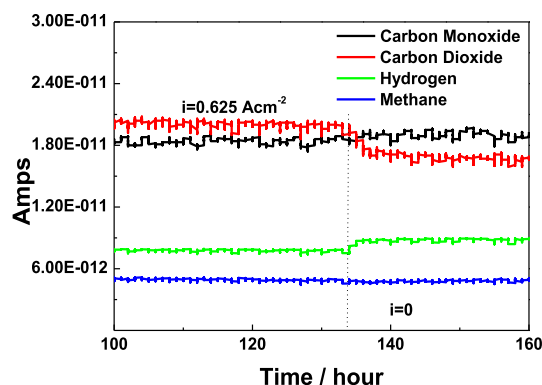


Fig. 3. Characterization of the cell composition at a current load of  $0.625 \text{ A cm}^{-2}$  and open circuit state.

open circuit state, and the  $\text{CO}_2$  concentration drops and levels off. It can thus conclude that  $\text{H}_2$  and  $\text{CO}$  have been consumed at the discharging condition. The oxidation of  $\text{CO}$  producing  $\text{CO}_2$  more presumably stems from the WGSR from a kinetic viewpoint. However, the 4%  $\text{CH}_4$  in fuel remains invariant in the entire process as can be seen in Fig. 3.

The gas composition is also detected at a fixed point of 350 h as displayed in Fig. 4, where the results from both the two states show strong methane signals, indicating the methane reforming must have been restrained the sulfur exposure. Therefore, the oxidation of  $\text{H}_2$  and the WGSR take advantages over methane reforming at the cell operational conditions. The specific evolution of each gas fraction inside the anode part can be merely understood in terms of SOFC modeling study [14]. Since the mixture of  $\text{H}_2$ – $\text{CO}$  cannot

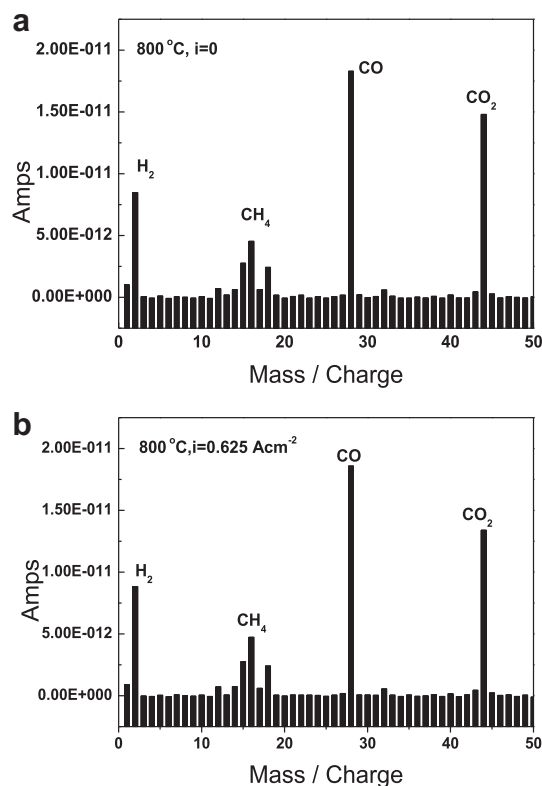


Fig. 4. Characterization of the cell composition at a current load of  $0.625 \text{ A cm}^{-2}$  at the point of 350 h.

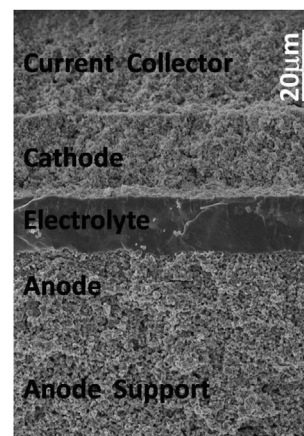


Fig. 5. Post-mortem microstructural observation of the cell after stable measurement.

release sulfur poisoning effects [11], steam in fuels plays a critical part of cutting down the effects of impurity.

The suppression of sulfur influences on the cell may be thus related to interactions between sulfur and steam involved reactions. On the one hand, it has been predicted that steam has the ability to remove the adsorbed sulfur atom on the  $\text{Ni}(100)$  [21]. For another, it is thermodynamically favorable for the oxidation of sulfur atom, producing some gaseous sulfoxides. Post-mortem microstructure of the cell has been carried out as shown in Fig. 5. The interfaces of electrodes and electrolyte are intact. The distribution of the pores in the anode is uniform, and no cluster or agglomeration emerges all through the electrodes. Hence, the cell remains invulnerable to the syngas containing 2 ppm  $\text{H}_2\text{S}$  due to the steam in syngas counteracting the sulfur poisoning impacts. Nevertheless, the presence of  $\text{H}_2\text{S}$  inhibits methane internal reforming.

#### 4. Conclusion

Electrochemical performance and long-term durability of a solid oxide fuel cell are investigated with a syngas containing 2 ppm  $\text{H}_2\text{S}$ . The mixed fuels are analyzed using a mass spectrometer to interpret the specific internal reforming that takes place with and without current passing the cell, and then the inhibition of sulfur contaminating the cell is discussed.

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